PHY 341/641 Thermodynamics and Statistical Mechanics
MWF: Online at 12 PM & FTF at 2 PM

Record!!!

Discussion for Lecture 26:

Quantum effects in statistical mechanics

Reading: Appendix A and Chapter 7

1. **Statistical mechanics of photons as Bose particles**
2. **Notion of density of states for photon states**
3. **Black body radiation**

21	Mon: 03/22/2021	Chap. 6.1 & 6.5	Microcanonical and canonical ensembles		
22	Wed: 03/24/2021	Chap. 6.1-6.2	Canonical distributions	#18	03/26/2021
23	Fri: 03/26/2021	Chap. 6.1-6.7	Canonical distributions	6.49	03/29/2021
24	Mon: 03/29/2021	Chap. 6.1-6.7	Canonical distributions	#20	03/31/2021
25	Wed: 03/31/2021	App. A & Chap. 7.1	Quantum mechanical effects	#21	04/02/2021
26	Fri: 04/02/2021	Chap. 7.1-7.2	Quantum mechanical effects		

Your questions – To be answered on Friday --

From Kristen -- 1. Could you explain why in this case we keep the mu dN term (equation 7.3)? 2. Why must Z be an integer in the example given in the beginning of section 7.2? 3. Could you explain what the quantum volume represents?

From Rich -- How do you calculate Zint for equation 7.10? Could you breakdown and better explain the (e-u)/kT phrase of the Fermi-Dirac and Bose-Einstein distributions?

From Chao –

The grand partition function for this single-site system has just two terms:

$$\mathcal{Z} = 1 + e^{-(\epsilon-\mu)/kT}. \qquad (7.9)$$

From Michael -- How do we distinguish the Gibbs sum/grand partition function from other partition functions we have learned about thus far, and when would we use it exactly? What exactly do the Fermi-Dirac and Bose-Einstein Distributions tell us?

From Parker -- What is the meaning behind degenerate energy levels that are equivalent in quantum mechanics as they are linearly independent, but are counted separately in statistical mechanics?

Summary of results from Wednesday --

Experimentally observed properties of Bose and Fermi particles --

Bose particles have integer *s*. It is observed that non interacting identical Bose particles are symmetrical under particle swapping – $\Psi(1,2)=\Psi(2,1)$. In terms of single particle states

$$\Psi_{Bose}(1,2)=\sqrt{\frac{1}{2}}\left(\Psi_A(1)\Psi_B(2)+\Psi_A(2)\Psi_B(1)\right)$$

Fermi particles have half integer *s.* It is observed that non interacting identical Fermi particles are anti-symmetrical under particle swapping – $\Psi(1,2)=-\Psi(2,1)$. In terms of single particle states

$$\Psi_{Fermi}(1,2)=\sqrt{\frac{1}{2}}\left(\Psi_A(1)\Psi_B(2)-\Psi_A(2)\Psi_B(1)\right)$$

$$\Psi_{Bose}(1,2) = \sqrt{\frac{1}{2}}\left(\Psi_A(1)\Psi_B(2) + \Psi_A(2)\Psi_B(1)\right)$$

$$\Psi_{Fermi}(1,2) = \sqrt{\frac{1}{2}}\left(\Psi_A(1)\Psi_B(2) - \Psi_A(2)\Psi_B(1)\right)$$

Conclusions for properties of non interacting identical Bose particles ➔ Many Bose particles may occupy the same quantum state

- Explains behavior of quanta of electromagnetic radiation (photons)
- Explains "Bose condensation"

Conclusions for properties of non interacting identical Fermi particles ➔ A quantum state may accommodate 1 or 0 Fermi"

- Explains behavior of electrons in an ideal metal

Consider the case of Bose particles. In this lecture we will focus on photon particles from quantum electromagnetic rays. It is reasonable to assume that the photon particles are non-interacting.

We learned that for Bose statistics, any number of particles can occupy each state. For photons the total number of particles is not fixed. For a state of energy $\epsilon \geq 0$, in thermal equilibrium at temperature T, the partial single particle partition function is given by $(\beta = 1/kT)$

$$Z_1(\epsilon, T) = \sum_{n=0}^{\infty} e^{-n\beta\epsilon} = 1 + e^{-\beta\epsilon} + e^{-2\beta\epsilon} + e^{-3\beta\epsilon} + ... = \frac{1}{1 - e^{-\beta\epsilon}}$$

Digression on geometric summation:

$$Z_1(\epsilon,T)=\sum_{n=0}^{\infty}e^{-n\beta\epsilon}=1+e^{-\beta\epsilon}+e^{-2\beta\epsilon}+e^{-3\beta\epsilon}+....=\frac{1}{1-e^{-\beta\epsilon}}$$

Proof:

$$e^{-\beta\epsilon}\sum_{n=0}^{\infty}e^{-n\beta\epsilon}=\sum_{n=0}^{\infty}e^{-n\beta\epsilon}-1$$

$$\Rightarrow\left(1-e^{-\beta\epsilon}\right)\sum_{n=0}^{\infty}e^{-n\beta\epsilon}=1 \quad \text{or} \quad \sum_{n=0}^{\infty}e^{-n\beta\epsilon}=Z_1(\epsilon,T)$$

Note that it is interesting to ask the question, for a given single particle energy ϵ_s what is the average occupancy $\langle n_s \rangle$

$$\langle n_s \rangle=\frac{\sum_{n=0}^{\infty}ne^{-n\beta\epsilon_s}}{Z_1(\epsilon_s,T)}=\frac{1}{e^{\beta\epsilon_s}-1}$$

Partition function for ensemble of photons at equilibrium at temperature T and having characteristic energies ε_a, ε_b, ε_c, …..

$$Z(T) = Z_1(\epsilon_a, T) Z_1(\epsilon_b, T) Z_1(\epsilon_c, T) \ldots = \frac{1}{1-e^{-\beta\epsilon_a}} \frac{1}{1-e^{-\beta\epsilon_b}} \frac{1}{1-e^{-\beta\epsilon_c}} \ldots..$$

$$\ln Z(T) = -\sum_s \ln\left(1-e^{-\beta\epsilon_s}\right)$$

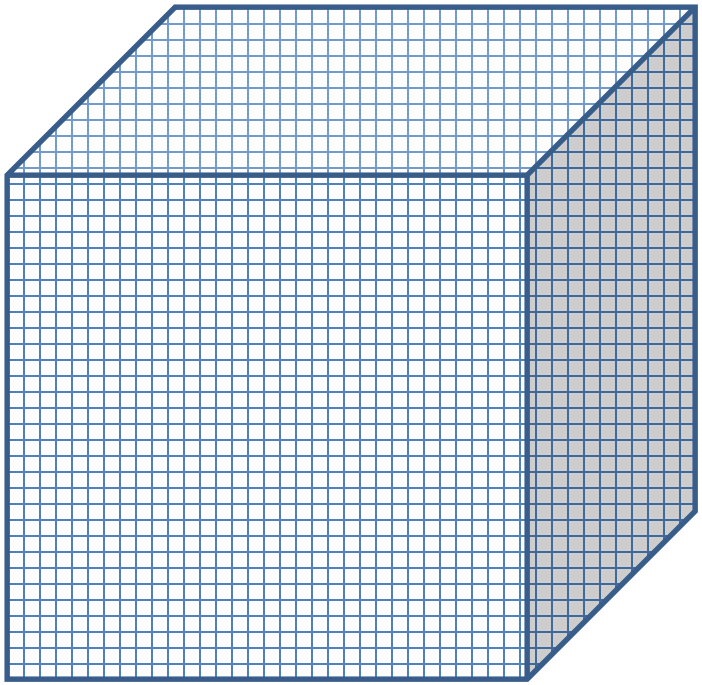
In practice, the state energies ϵ_s form a continuum

$$\sum_s \rightarrow \int d\epsilon \; g(\epsilon)$$ where $g(\epsilon)$ denotes the density of states

It can be shown that for a system of photons within a volume V, the density of photons at energy ϵ is

$$g(\epsilon) = \frac{V\epsilon^2}{\pi^2\hbar^3 c^3}$$ where c is the speed of light in vacuum.

Electromagnetic modes within volume V=L^3



$$\epsilon = \frac{hc}{L}\sqrt{n_x^2 + n_y^2 + n_z^2}$$

for integers n_x, n_y, n_z

In the limit that $L \to \infty$, ϵ becomes continuous.

Note that g(ϵ) accounts for two polarizations of photons.

Average internal energy for photons in equilibrium at temperature $T = 1/(k\beta)$

$$\langle U \rangle = \int d\epsilon \; g(\epsilon)\, \epsilon \langle n(\epsilon) \rangle \qquad g(\epsilon) = \frac{V\epsilon^2}{\pi^2 \hbar^3 c^3}$$

$$= \frac{V}{\pi^2 \hbar^3 c^3} \int d\epsilon \; \epsilon^3 \frac{1}{e^{\beta\epsilon} - 1} = \frac{8\pi V (kT)^4}{h^3 c^3} \underbrace{\int_0^\infty dx \frac{x^3}{e^x - 1}}_{= \frac{\pi^4}{15}}$$

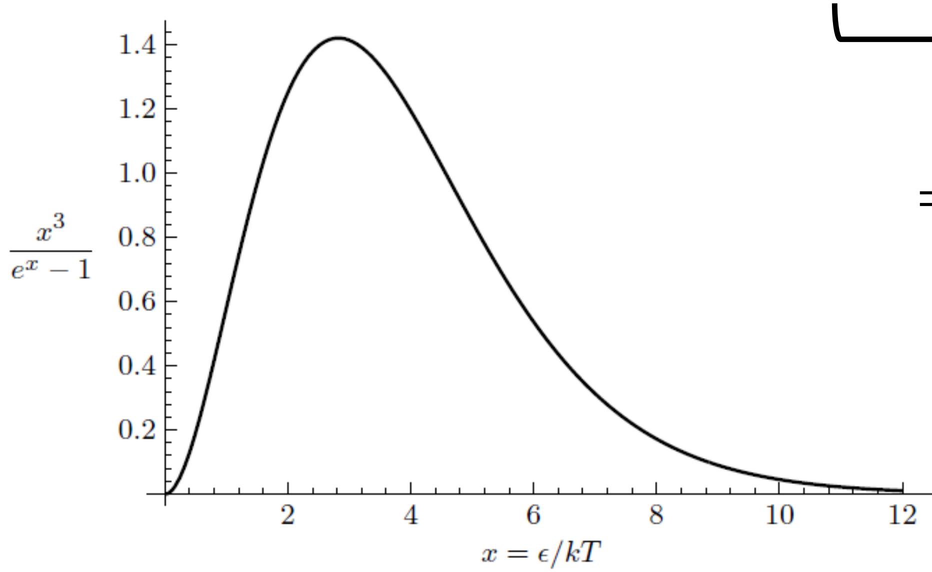


Figure 7.19. The Planck spectrum, plotted in terms of the dimensionless variable $x = \epsilon/kT = hf/kT$. The area under any portion of this graph, multiplied by $8\pi(kT)^4/(hc)^3$, equals the energy density of electromagnetic radiation within the corresponding frequency (or photon energy) range; see equation 7.85. Copyright ©2000, Addison-Wesley.

$$\langle U \rangle = V \frac{8\pi^5 (kT)^4}{15 (hc)^3}$$

Historical importance of the formula for Blackbody radiation

Max Planck 1858-1947

A blackbody means an idealized opaque (non-reflective) material which can absorb and emit electromagnetic radiation. If the body has an equilibrium temperature T, the energy associated with the blackbody is <U>.

$$\langle U \rangle = V \frac{8\pi^5 (kT)^4}{15(hc)^3}$$

Heat capacity and entropy associated with the equibrium blackbody radiation

$$\langle U \rangle = V \frac{8\pi^5 (kT)^4}{15(hc)^3}$$

Heat capacity: $$C_V = \left(\frac{d\langle U \rangle}{dT} \right)_V = V \frac{32\pi^5 k^4 T^3}{15(hc)^3}$$

Entropy: $$S(T) = \int_0^T \frac{C_V(T')}{T'} dT' = V \frac{32\pi^5 k^4 T^3}{45(hc)^3}$$

Checking results

Helmholtz free energy:

$$F = -kT \ln Z(T) = kT \sum_s \ln\left(1 - e^{-\beta\epsilon_s}\right)$$

In practice, the state energies ϵ_s form a continuum

$$\sum_s \rightarrow \int d\epsilon \; g(\epsilon) \qquad \text{where } g(\epsilon) \text{ denotes the density of states}$$

$$g(\epsilon) = \frac{V\epsilon^2}{\pi^2 \hbar^3 c^3}$$

$$F(T) = kT \frac{V}{\pi^2 \hbar^3 c^3} \int_0^\infty d\epsilon \; \epsilon^2 \ln\left(1 - e^{-\beta\epsilon}\right) = -\frac{8\pi V (kT)^4}{h^3 c^3} \frac{\pi^4}{45}$$

$$= U - TS$$

More modern evidence of blackbody radiation from the remnant radiation from the initiation of the universe measured by the cosmic background explorer satellite.

Average internal energy for photons in equilibrium at temperature $T = 1/(k\beta)$

$$\langle U \rangle = \int d\epsilon \; g(\epsilon) \; \epsilon \langle n(\epsilon) \rangle$$

$$= \frac{V}{\pi^2 \hbar^3 c^3} \int d\epsilon \; \epsilon^3 \frac{1}{e^{\beta\epsilon} - 1} = \frac{8\pi V (kT)^4}{h^3 c^3} \int_0^\infty dx \frac{x^3}{e^x - 1}$$

It is convenient to express the photon energy as $\epsilon = hf$ --

$$\langle U \rangle = \frac{Vh^4}{\pi^2 \hbar^3 c^3} \int df \; f^3 \frac{1}{e^{\beta hf} - 1} = \frac{8\pi Vh}{c^3} \int_0^\infty df \frac{f^3}{e^{\beta hf} - 1}$$

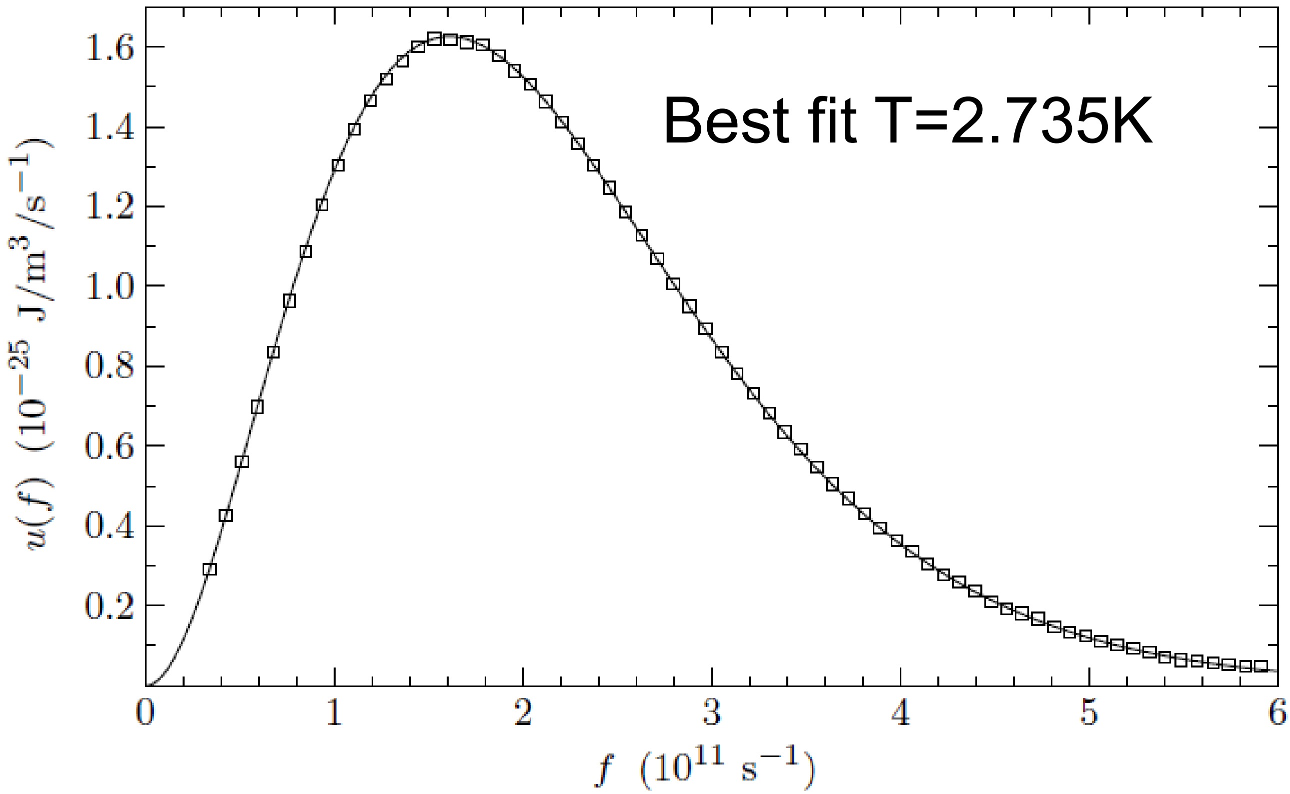
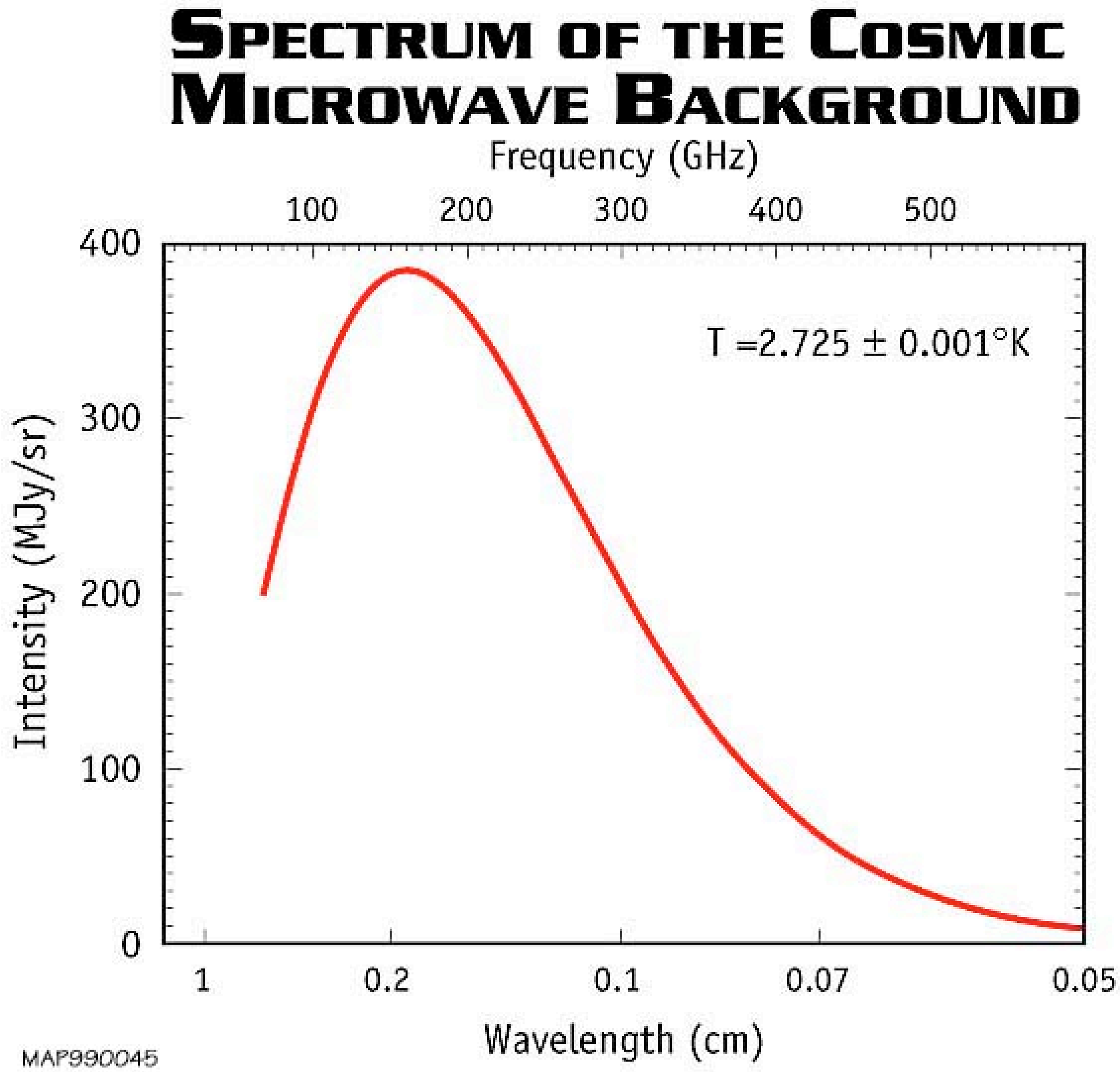


Figure 7.20. Spectrum of the cosmic background radiation, as measured by the *Cosmic Background Explorer* satellite. Plotted vertically is the energy density per unit frequency, in SI units. Note that a frequency of 3×10^{11} s^{-1} corresponds to a wavelength of $\lambda = c/f = 1.0$ mm. Each square represents a measured data point. The point-by-point uncertainties are too small to show up on this scale; the size of the squares instead represents a liberal estimate of the uncertainty due to systematic effects. The solid curve is the theoretical Planck spectrum, with the temperature adjusted to 2.735 K to give the best fit. From J. C. Mather et al., *Astrophysical Journal Letters* **354**, L37 (1990); adapted courtesy of NASA/GSFC and the COBE Science Working Group. Subsequent measurements from this experiment and others now give a best-fit temperature of 2.728 ± 0.002 K. Copyright ©2000, Addison-Wesley.

From NASA website --
https://wmap.gsfc.nasa.gov/universe/bb_tests_cmb.html



Next –

What happens with Boson particles with a fixed number?

What happens with Fermi particles with a fixed number?